

Synthesis of *p*-cymene from limonene, a renewable feedstock

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Abstract

Highly selective limonene conversions to *p*-cymene in short reaction times were achieved under “solvent free” conditions over mesoporous silica–alumina supports heated by microwave irradiation. An increase in the silica content of these mixed oxides led to increases in the specific surface area, porosity (pore size and volume) and the surface acidity. The conversion and selectivity of limonene to *p*-cymene under microwave irradiation was also found to rise as the silica content in these mixed oxides was increased. By careful choice of the solid and reaction parameters the activities for the conversion of limonene and selectivity to *p*-cymene (used as an intermediate in fine chemical syntheses) could be fine tuned. Results are presented under both dry media and reflux conditions.

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1. Introduction

The importance of *p*-cymene is due to its utilisation as an intermediate in industrial fine chemicals syntheses for fragrances, flavourings, herbicides, pharmaceuticals, *p*-cresol production, syntheses of not nitrated musk's (i.e. tonalide), etc. [1–4]. Conventional preparation of *p*-cymene is based on the Friedel–Crafts alkylation of petroleum derivatives: benzene with methyl and isopropyl halides using AlCl_3 as an acid catalyst, or toluene with isopropyl alcohol [5]. At present approximately 4000 tons of *p*-cymene are produced annually [6]. However, due to their low selectivities to *p*-cymene, these alkylations invariably produce mixtures of *ortho* and *para* isomers, with the subsequent need for costly separation processes. Moreover, the use of highly toxic substances such as benzene or toluene and AlCl_3 are becoming more restricted by environmental legislation in industrialised countries. Thus, new pathways that avoid the continued use of these toxic reagents should be found.

Limonene is a low cost, low toxicity biodegradable terpene present in agricultural wastes derived from citrus peels. As such

this reagent can be considered as an economical renewable feedstock. Limonene has a six member ring that can be aromatised, making it a suitable candidate to substitute the aromatic intermediates produced from fossil fuels or petroleum derivatives employed at present.

A series of commercial silica–alumina mixed oxides, supplied by Sasol, whose compositions ranged from 1 to 40 wt.% silica were employed in this study. Since the conversion of limonene to *p*-cymene is catalysed by acid sites, Al-OH and Al^{3+} on the surface of these materials are crucial for their reactivity, with Brønsted acidity related to their surface –OH and Lewis acidity related to electron accepting Al^{3+} sites [7]. The textural and acid characteristics of these mixed oxides were determined and related with their activity to transform limonene to *p*-cymene under microwave irradiation in both dry media and reflux conditions.

Microwave irradiation has proven to be an efficient technology as an alternative energy source to conventional heating, our group pioneering this field [8]. In chemical reactions the homogeneous nature of this energy source compared to conventional heating can be advantageous [8,9]. Additionally, the accelerated heating rate experienced during microwave irradiation can be particularly useful in reducing the overall reaction times, that may influence the product selectivity [10].

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2. Experimental

2.1. Raw materials

The catalytic supports used in this study were prepared by a patented procedure [11], based on the acid hydrolysis of aluminium hexalate dissolved in hexanol (6 wt.%) and orthosilicic acid (3 wt.%) mixtures. The resulting gel (pseudo-boehmite) is dried with pressurised air and subsequently heat-treated at 180 °C for 5 h with autogenous pressure. Varying the amount of orthosilicic acid different amounts of silica may be incorporated into the mixed oxide. In this study silica contents ranging from 1 to 40 wt.% were employed, designated as SIRAL 1 to SIRAL 40, accordingly.

D-limonene supplied by Sigma–Aldrich (99.9%) was used in the reactions without any further purification. The extractions of the reactant and product mixtures were made using ethanol since this was shown to be an adequate solvent for all the compounds likely to be present before and after reaction.

3. Characterisation

The texture of the mixed oxides: specific surface area and pore volume were analysed by adsorption/desorption of nitrogen at –196 °C, in a Tristar apparatus from Micromeritics. Before measurement the samples were outgassed overnight at 300 °C to a vacuum of less than 10^{-4} Torr to ensure that they were clean, dry and free from any loosely adsorbed species. All subsequent calculations were made subject to the outgassed weight of the sample. The BET method was used to determine the specific surface areas (S_{BET}) from the adsorption data in the linear portion of the isotherm located in the relative pressure range of 0.05–0.30 p/p°, typical for this type of sample [12]. The mesopore size distributions were calculated from the desorption branch of the corresponding nitrogen isotherm using the Kelvin equation and the BJH method with the parameters for the thickness of the adsorbed layers from the Harkins–Jura equation, chosen since this employed a metal oxide as the non-porous standard [13].

The total acidities of the solids were analysed from their ammonia adsorption capacities, determined on a Micromeritics ASAP 2010 device. For these measurements the samples were first outgassed overnight at 300 °C to a vacuum of about 10^{-4} Torr to ensure that the solids were clean dry and free of any loosely bound adsorbed species. The ammonia adsorption isotherms at 30 °C were subsequently determined up to a pressure of about 350 Torr, thus obtaining the total chemisorption plus physisorption capacities. The samples were then outgassed at 30 °C to remove the loosely bound physisorbed species and a second adsorption isotherm at 30 °C determined to measure the physisorption capacity of the sample. The chemisorption capacity was calculated from the differences in the ammonia uptakes between the first and second isotherms. The total acidities were subsequently calculated assuming that each molecule of ammonia reacted with one acid site [14,15].

Pyridine adsorption coupled with infrared analysis was used to determine qualitatively the Lewis and Brønsted acid sites of the mixed oxide supports. The solids were made into self-

supporting discs and then outgassed at 300 °C for 5 h under high vacuum to remove any loosely bound species from the surface. The discs were then contacted with pyridine vapour at room temperature for 30 min and subsequently outgassed at room temperature in order to remove the weakly adsorbed species. From the infrared spectra the Lewis and Brønsted acid sites were qualitatively analysed from their typical adsorption peaks at 1455 and 1545 cm^{-1} , respectively [16].

3.1. Catalytic reaction

Due to the poor reproducibility of standard multimode microwave ovens for chemical reactions, in this study a focalised monomodal system was employed. The apparatus, a Synthwave 402 from Prolabo, allows the programming and measurement of the sample temperature by infrared detection. The reactions were carried out under both dry media and reflux conditions, the latter in order to simulate an industrial application where greater amounts of reactant can be used with much lower catalyst to reactant ratios.

Microwave induced reactions in dry media, are considered a clean technology as they avoid the use of solvents. This technology can also be used as an efficient and economic method for the fast screening of catalysts. For the dry media reactions 50 μl of limonene were physically mixed with 200 mg of solid. These mixtures were then placed in a glass reactor and subsequently irradiated at maximum power output of 300 W for fixed periods of time: 5, 10 or 20 min.

When the reaction was carried out in reflux conditions 500 mg of solid was mixed with 5 ml of limonene. This mixture was heated to a maximum temperature of 165 °C for 10 or 20 min, with the power output of the microwave oven controlled automatically to avoid overheating of the reaction mixture. The final temperature was chosen to be slightly lower than the boiling points of the reactant and products (limonene 175 °C, *p*-cymene 177 °C) in order to control the reaction. Additionally a reflux column was used to ensure that there was no loss of materials.

In both cases at the end of the experiments the reaction mixtures were allowed to cool and the reactants and products then extracted by dissolution in ethanol. These mixtures were subsequently analysed by GC–MS (Hewlett Packard 5890 series II GC with a 25 m methyl silicone capillary column heated in a helium flow from 50 to 170 °C at 6 °C min^{-1} , coupled to a Hewlett Packard series 5971 mass spectrometer). To ensure the reproducibility of the results the injector and detector were heated to 180 and 250 °C, respectively to avoid condensation of the mixtures.

Following the extraction of the reaction products with ethanol, the catalytic activities of the samples were redetermined using the same protocols as described above. In this way it was possible to ascertain if the materials had suffered any loss in their catalytic activities or selectivities.

4. Results and discussion

It has been previously proposed that the available surface area coupled with the accessibility to the active acid sites play

important roles in controlling the catalytic process in this reaction [17]. The results of specific surface areas, pore volumes and average mesopore diameters of the solids used in this investigation are summarised in Table 1. The nitrogen adsorption/desorption isotherm for SIAL 1 was of type IV with a well-defined plateau at high relative pressures, characteristic of a mesoporous solid. The hysteresis loop was of type H1 according to the IUPAC classification [13], corresponding to porous materials consisting of agglomerates of regular shape with narrow mesopore size distributions. As the silica content was increased there was a progressive increase in the specific surface area, mesopore volume and average mesopore diameters. This shift to wider pores was evidenced by a widening of the hysteresis loop between the adsorption and desorption branches. Furthermore, in solids with the highest silica contents the plateau at higher relative pressures became less well defined as the pore sizes shifted into the narrow macropore range. From the isotherms obtained for SIAL 1 and SIAL 40 presented in Fig. 1a the change in the hysteresis loop due to the widening of the pores may be appreciated while the upward displacement of the curve with the increased silica content was indicative of the greater specific surface area. The other samples with intermediate silica contents, not shown here for clarity, gave rise to adsorption/desorption curves that lay between these two extremes.

The mesopore size distributions of SIAL 1 and SIAL 40 are presented in Fig. 1b. Although in the case of SIAL 1 the curve appears to show a trimodal mesopore size distribution, it should be noted that the peak found at a pore diameter of 3.7 nm was due to the sudden closure of the desorption hysteresis loop at a relative pressure close to 0.42. This peak, commonly found with many materials, is due to the breakage of the liquid meniscus and as such is an artefact of the measurement technique and should not be confused with the presence of a well-defined narrow mesoporosity in pore diameters close to 3.7 nm. However, this peak does indicate the presence of narrower mesopores in the material. From the pore size distribution curve for SIAL 40, shown in Fig. 1b, the shift to wider pores as the silica content in these mixed oxides was increased may be clearly appreciated.

From the ammonia adsorption results presented in Fig. 2 it may be observed how the total acidities of the solids rose as the silica content in these mixed oxides was increased. However, it should be noted that these increases in acidity were not directly proportional in either per gram or per square metre basis of chemisorbed ammonia versus silica content. The non-linearity

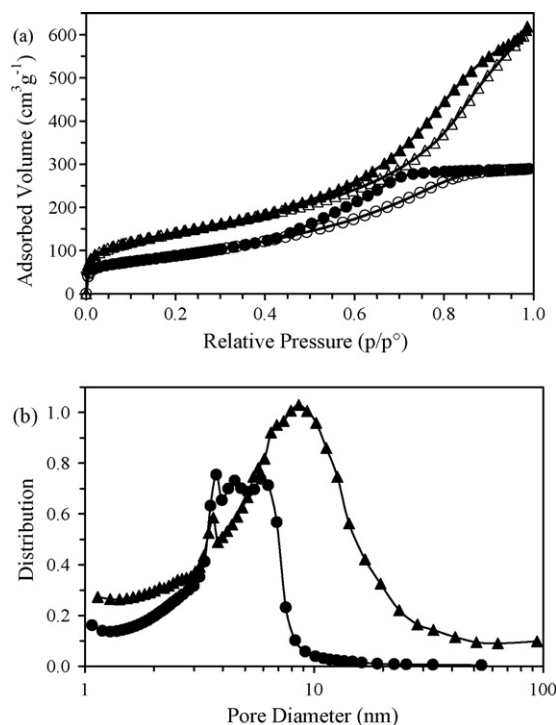


Fig. 1. (a) Nitrogen adsorption/desorption isotherms for SIAL 1 (○ ●) and SIAL 40 (△ ▲). (b) Pore size distributions from the desorption branches of the nitrogen isotherms of SIAL 1 (●) and SIAL 40 (▲).

of these curves was probably due to the reported encapsulation process suffered by the solids where the surface silica composition was much higher than the bulk composition as analysed by XPS [18]. The FTIR spectra after pyridine adsorption for all the samples are presented in Fig. 3. A qualitative analysis of these curves clearly indicated that as the silica contents in the mixed oxides were increased the peak intensities at the characteristic positions for both Lewis and Brønsted acidity rose.

Microwave irradiation was chosen for its characteristics of rapid and homogeneous heating. Previous studies with this heating source have demonstrated surprising conversions and selectivities in various reactions [19,20]. The transformation of

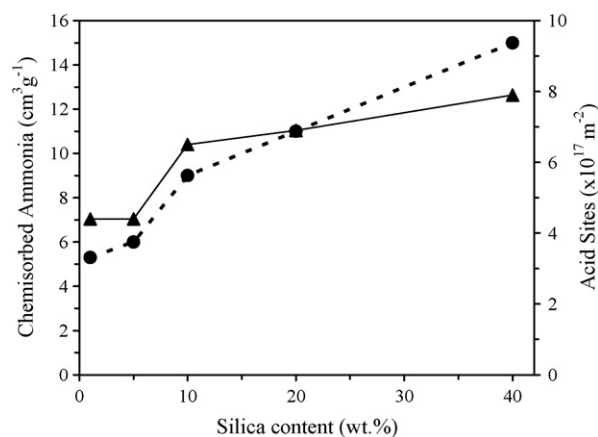


Fig. 2. Ammonia adsorption as cm³ g⁻¹ (●) and number of acid sites m⁻² (▲) vs. silica content of the mixed oxides.

Table 1
Textural properties of the mixed oxides

Sample	Specific surface area (S_{BET}) (m² g⁻¹)	Pore volume (cm³ g⁻¹)	Average mesopore diameters (nm)	
SIAL 1	321	0.45	4.5	5.8
SIAL 5	364	0.57	4.8	5.9
SIAL 10	422	0.59	4.8	6.8
SIAL 20	432	0.68	5.4	9.4
SIAL 40	506	0.95	5.8	12.7

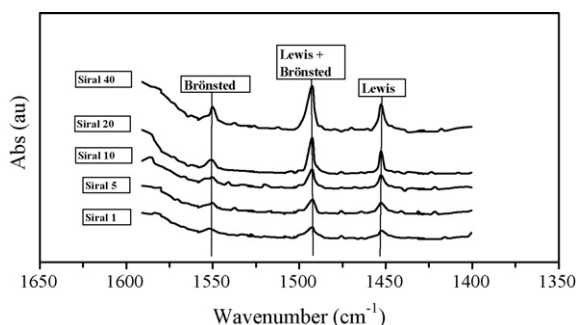
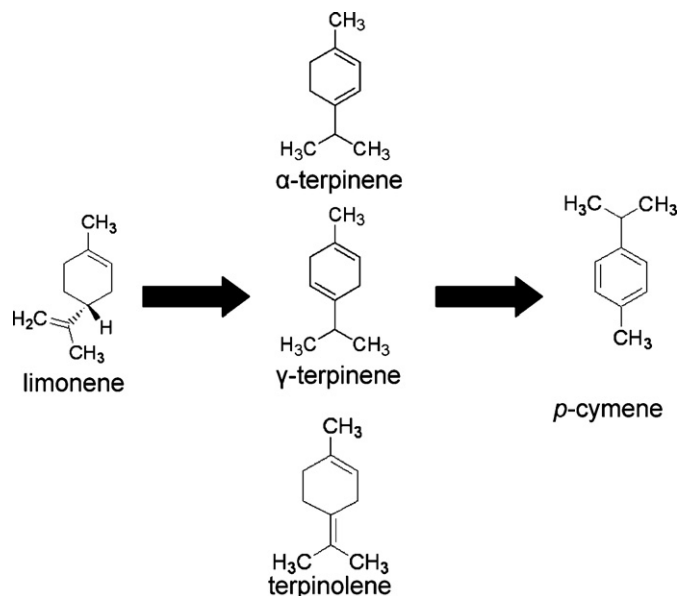


Fig. 3. FTIR spectra of solids after pyridine adsorption at 30 °C.

limonene and other terpenes has been previously attributed to their reaction with acid sites that protonate the unsaturated molecules, along with the possibility of dehydrogenation or polymerisation. The reaction mechanism of limonene and other terpenes in the presence of solid acids has been related to an initial isomerisation on acid sites, followed by dehydrogenation of these intermediates to give *p*-cymene, disproportionation (slow reaction, compared to isomerisation or dehydrogenation, due to the need for two molecule intermediates) and in some cases polymerisation [17].

In agreement with our results the mechanism involves adsorption of the extracyclic double bond of limonene on the acid site, forming a primary carbonium ion, followed by displacement of the proton to form the more stable tertiary carbonium ion from which terpinolenes, or terpinenes are formed [21]. Intermediates formed from the adsorption of the endocyclic double bond are unlikely, due to steric hindrance. The subsequent dehydrogenation of the intermediates produced after isomerisation has been found previously [4]. The reactants and products found with microwave irradiation of limonene are shown in Scheme 1.

The results obtained with microwave irradiation of limonene are presented in Table 2. Since the reaction is catalysed by the



Scheme 1. Reactant and products found with microwave irradiation of limonene.

acid sites the higher activity as the number and accessibility of the surface acid sites rose with increased silica content was to be expected. Although greater activities were found as the total acidity was increased (measured by ammonia adsorption, Table 1), since there was an increase in both Lewis and Brønsted acid sites, indicated by pyridine adsorption results as the silica content was augmented, presented in Fig. 3, no direct correlation could be made with either type of site.

From the evolution of the reaction on SIRAL 1, shown in Fig. 4, it may be seen, that only α- and γ-terpinene, γ-terpinolene and *p*-cymene were found as products of the reaction. However, no compounds such as menthanes or menthenes, produced by disproportionation or polymerisation, were detected. From the results presented in Fig. 4a and b and

Table 2
Limonene conversion and selectivities under dry media conditions

Sample	Time (min)	Conversion (%)	Selectivity			
			α-Terpinene (%)	γ-Terpinene (%)	α-Terpinolene (%)	<i>p</i> -Cymene (%)
SIRAL 1	5	15	85	0	15	0
	10	56	52	14	0	34
	20	100	0	0	0	100
SIRAL 5	5	42	60	12	21	7
	10	63	27	25	0	48
	20	100	0	0	0	100
SIRAL 10	5	65	48	11	31	10
	10	69	15	0	14	71
	20	100	0	0	0	100
SIRAL 20	5	88	31	6	15	48
	10	100	0	0	0	100
	20	100	0	0	0	100
SIRAL 40	5	93	0	0	3	87
	10	100	0	0	0	100
	20	100	0	0	0	100

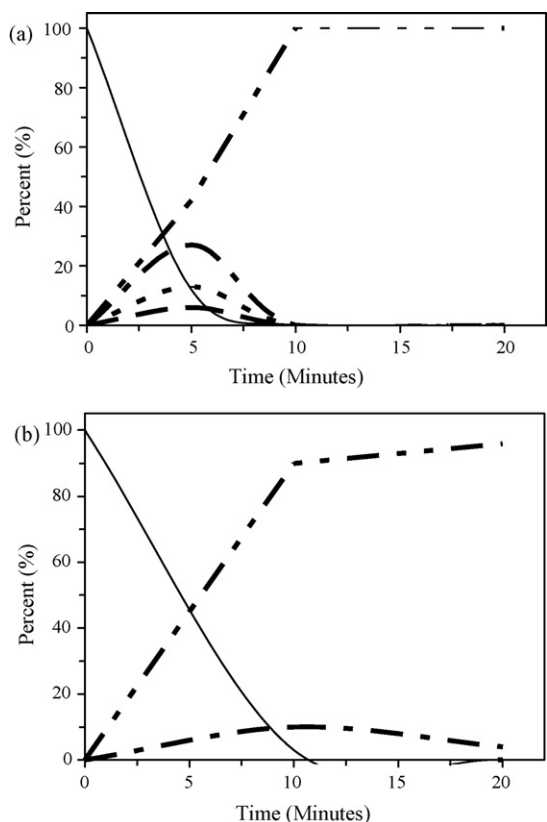


Fig. 4. Reactant and product distributions vs. time for (a) Siral 1 in dry media and (b) Siral 20 under reflux: limonene (—), α -terpinene (---), γ -terpinene (---), α -terpinolene (---) and *p*-cymene (---).

Table 2 it should be noted that the selectivity to *p*-cymene increased with both longer irradiation times and increased silica contents in the supports. For the two samples with the highest silica contents reaction times of just 10 min gave selectivities to *p*-cymene of greater than 90%. Since these samples had the most acid centres, calculated on both per gram or per $\text{m}^2 \text{g}^{-1}$ basis, it would appear that the selectivity to *p*-cymene was due to the rapid aromatisation of the intermediates produced by isomerisation over the acid centres. Although conversion of limonene to *p*-cymene over Lewis acid sites with conventional heating has been previously observed, the much longer reaction times necessary to increase the overall conversion (3 h) leads to reduced selectivities due to the formation of undesirable mentanes, etc. [22].

The evolution of temperature against time for these mixtures during the initial 5 min was similar for all the tested solids, reaching a final temperature of ca. 163°C , with differences of less than 2°C among them. An initial sharp rise in temperature during the first minute of irradiation was followed by a slower but continuous rise in temperature up to the end of the reaction, as shown in Fig. 5a. In the experiments of 10 and 20 min duration similar tendencies were found with the final temperatures reaching 195 and 227°C , respectively. Thus, the different compositions of the supports had no effect on the heating rate of the samples with microwave irradiation.

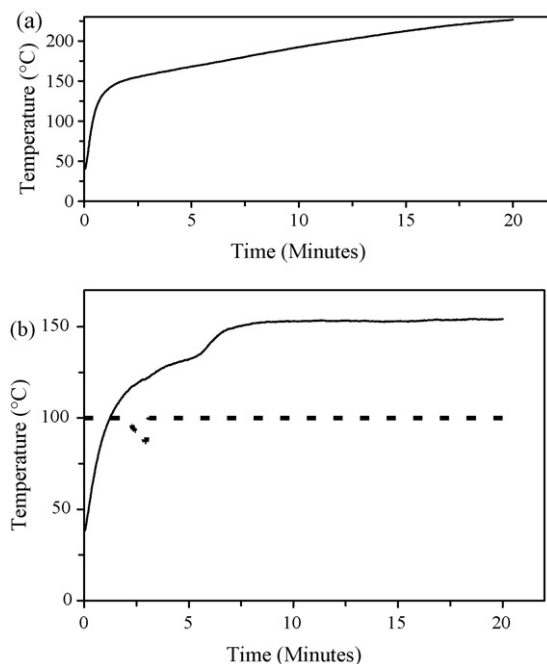


Fig. 5. Temperature variation vs. time in (a) dry media and (b) reflux for Siral 20. The dashed line in the reflux experiment indicates the power output of the microwave reactor.

When the experiments were carried out in reflux conditions a maximum temperature of 165°C was set. Thus, although all the solids behaved similarly the evolution of temperature increase was different to that found in the dry media conditions. After an initial rapid rise in temperature of about 1°C s^{-1} the power was automatically reduced causing a subsequent decrease in the heating rate at about 120°C , followed by a slower controlled rise towards the desired final temperature, presented in Fig. 5b.

The evolution of the products obtained after irradiation at 5, 10 and 20 min in dry media for all the solids are shown in Table 2. From these results it may be observed that with longer irradiation times both the limonene conversion and the selectivity to *p*-cymene increased for all solids. It should also be noted that the conversions and selectivities were greater as the amount of silica in the solids was increased. The only intermediate products of reaction found were α -terpinene, α -terpinolene, γ -terpinene (from isomerisation) and *p*-cymene (from dehydrogenation), with no other products found, such as those from disproportionation.

In dry media the reaction with SIRAL 1 did not exceed 60% conversion, even after 10 min of irradiation. This result was indicative of a slower conversion probably due to both the lower acidity and specific surface area of this material. The conversions rose as the quantity of silica in the samples was increased since this caused a rise in both the number of acid sites and specific surface area of these mixed oxides. The increased activity of the solids with higher silica contents lead to 100% conversions after only 10 min of irradiation for both SIRAL 20 and SIRAL 40.

The selectivity to *p*-cymene also rose as the irradiation time and silica content of the solids was increased. For the two

samples with the highest silica contents the selectivity to *p*-cymene was greater than 90% after 10 min of irradiation. These high conversions and selectivities are most probably due to the rapid aromatisation of the intermediates produced by isomerisation on the acid centres, as reported earlier with conventional heating although with much lower selectivities to those found here [22]. Under conventional heating, using acid solids in liquid phase, 100% conversions were obtained after 3 h at 150 °C. However, the highest selectivity to *p*-cymene was only 40%, with products of disproportionation and polymerisation also being found.

In order to carry out the reaction in conditions closer to those used industrially the two samples with the highest reactivities in dry media were chosen for further study in reflux conditions. The most important differences between the reaction conditions in dry media and reflux conditions are the final reaction temperature: 225 °C compared to 165 °C and the ratio between the reactants and the solid: 0.00025 and 0.01 ml g⁻¹, respectively. From the results shown in Table 3 it may be observed that the intermediate isomerisation product α -terpinene was only found for SIAL 20 and at a very low level (4%). Furthermore, 100% conversion of limonene to *p*-cymene was achieved with Sial 40 after only 10 min. The speed of the reaction when heated by microwave irradiation is possibly the reason for the high selectivities found, since the short reaction time necessary to attain these high conversions and selectivity to *p*-cymene avoid the formation of undesirable by-products such as mentanes (products of disproportionation) or polymers, that are found with the longer reaction times employed with conventional heating [23].

The industrial production of *p*-cymene is carried out by Friedel–Crafts alkylation's form benzene or toluene. Thus, although recent research has been carried out to make this process less toxic by the use of solid acids instead of the conventional homogeneously catalysed reaction [24], the selectivity was well below 100% and thus expensive separation techniques would still be required. Furthermore, under gas–solid conditions to alkylate toluene with isopropyl alcohol temperatures in excess of 300 °C are required and even then toluene conversions and selectivities to *p*-cymene of little more than 50% were attained [25]. In contradistinction the process presented here with microwave irradiation achieved selectivities of 100% in very short reaction times with the additional advantages of using limonene, a renewable feedstock, as reactant, whose toxicity is orders of magnitude lower than that of toluene or benzene.

Table 3
Limonene conversion and selectivities in reflux

Sample	Duration (min)	Conversion (%)	Selectivity	
			α -Terpinene (%)	<i>p</i> -Cymene (%)
SIAL 20	10	97	10	90
	20	100	4	96
SIAL 40	10	100	0	100
	20	100	0	100

5. Conclusions

These results illustrate that the use of microwave irradiation is particularly favourable for the production of *p*-cymene from limonene. This production method is of interest since it avoids the use of highly toxic feedstocks presently used for its manufacture such as: benzene, toluene and aluminium trichloride. The high conversions and excellent selectivity towards the desired product (*p*-cymene), avoiding undesirable by-products were believed to be due to the accelerated heating and reaction rates achieved with microwave irradiation. As the reaction is governed by the number and accessibility of the acid sites there was a clear relationship between the greater reactivities achieved with increased silica contents of these mixed oxides. Higher silica contents lead to greater specific surface areas, pore volumes and average pore sizes in addition to an increased number of acid sites. These effects were complementary since they caused a rise in both the number and accessibility of the active acid centres necessary for this reaction.

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